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25 YEAR RE-REVIEW

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GEOCHEMICAL EVOLUTION OF PETROLEUM

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Petroleum like any mineral or rock can not remain in the earth unchanged but undergoes certain transformations. The geochemical evolution of petroleum is concerned with the direction of these transformations. The nature of this evolution can be determined from theoretical thermodynamic considerations, laboratory experiments, and the relation between petroleum composition and its geological and geochemical environment.

An analysis of the thermodynamics of the chief processes that alter the constituents of petroleum leads to the following conclusions. In the absence of oxidizing agents, a mixture of paraffins, naphthenes and aromatics must be changed in a certain direction, viz. the decay and decyclisation of the naphthenes, the formation of paraffins and aromatics (with condensation of the latter up to the point of their maximum solubility), and as a general result, the "denaphthenisation" and "deparaffinisation" of the hydrocarbon mixture. These changes correspond to a decrease in free energy.¹

The results of laboratory experiments show that at low temperatures in the presence of aluminosilicate catalysts (including inactive clays) the following processes take place: (1) the decarboxylation of acids with the formation of hydrocarbons typical of petroleum, (2) decyclisation of naphthenes, (3) formation of paraffins as a result of the decyclisation of the naphthenes and condensed ring aromatic-naphthenic hydrocarbons, (4) separation of the side chains from these hydrocarbons, (5) alkylation of the aromatics, and (6) other processes. As a result, one observes the formation of light ends and a decrease in the specific gravity.¹

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Of the various relations between petroleum composition and the geological and geochemical environment, the effect of geologic age is most interesting because it suggests the general direction of the natural evolution of petroleum. Figure 1 presents the hydrocarbon composition (up to boiling points of 550°C)* of 65 crude oils from the following regions: Caucasus, Turkmenia, Sakhalin, California, Venezuela, Indonesia, Volga-Ural, North-American platform, Siberia, Emba, and Middle Asia. The data are all taken from the literature. Crude oils of paleozoic, mesozoic and cenozoic ages are indicated by different symbols.

Figure 1 shows that paleozoic oils containing more than 30 percent paraffins are located among mesozoic and cenozoic crudes containing more or less than this amount. On the basis of these same data, the average ratios of naphthenes to paraffins are: for cenozoic, 2.0, for mesozoic, 1.25, and for paleozoic, 0.6. Data on the hydrocarbon composition of the light ends gives the same picture. These data were obtained for crude oils from Rumania, Italy, California, Trinidad, Mid-Continent, Gulf Coast, and Mexico, and the average ratio between naphthenes and paraffins in the light ends (for 16 oils up to 200°C and for 10 oils up to 100°C) was determined. Figure 2 shows this ratio for crude oils, naphthas and light ends of paleozoic, mesozoic and cenozoic ages.

Figures 1 and 2 show that the cyclic constituents in petroleum generally decrease in concentration with an increase in geologic age. The older the petroleum is, the greater the content of paraffins and the less the naphthenes.

These alterations of petroleum with geologic age agree completely with what is predicted by thermodynamic considerations and what has been found by

* Note: The chief part of these analyses was done by the anilin method, but the procedure used is not essential to our present purpose.

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experimentation. Consequently, a correlation of thermodynamic and laboratory data and geochemical observations leads to the conclusion that the chief process in petroleum evolution in Nature is the transformation of petroleum from primarily a cyclical composition to a paraffinic composition (and finally into gaseous hydrocarbons). This process - the metamorphism of petroleum - is spontaneous because of the consequent decrease in free energy of the system and is accelerated by temperature and natural catalysts. In view of these circumstances it is appropriate to term the process as the "thermocatalytic metamorphism of petroleum."

The influence of temperature can be observed in the changes in the hydrocarbon composition of petroleum with depth. Table I lists average ratios based on data from the literature (for distillations up to 550°C) for naphthenes: paraffins for crude oils of the USSR.

TABLE I

Age	D e p t h (m)				
	less than 500	500-1000	1000-1500	1500-2000	More than 2000
Cenozoic	more than 30 (8)	5 (7)	2 (9)	1 (1)	0,5 (1)
Mesozoic	5 (4)	2 (4)	1 (2)	0,3 (1)	0,15 (1)
Paleozoic	1 (3)	1 (6)	0,8 (7)	0,5 (13)	-

Note: 1. All fractions have been rounded off to the nearest integer.

2. Numbers in parentheses give the number of samples analyzed.

The data of Table I show that the naphthene-paraffin ratio decreases with increasing depth for all geologic ages. Consequently, the influence of depth (and therefore, of temperature) on the hydrocarbon composition of petroleum

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is of the same kind as that of geologic time. The influence of temperature on petroleum composition can complement the effects of time. Therefore, considerably metamorphosed crudes occur in other ages than the paleozoic (see Figure 1). The age of the paleozoic, of course, is itself a sufficient condition for considerable metamorphism.

It is not clear, however, during what stage in the formation of petroleum that thermocatalytic metamorphism is important, i.e. during the occurrence of petroleum hydrocarbons as dispersed organic matter in the source beds or after the hydrocarbons have accumulated as oil pools. The metamorphism of dispersed organic matter cannot be doubted, but there is some evidence that indicates that considerable metamorphism also occurs within the pool.

In addition to thermocatalytic metamorphism, petroleum can also be oxidized and sulfurized under certain conditions. Many crudes with a high sulfur content are included in the group whose compositions were used in preparing figures 1 and 2. This fact, however, evidently does not interfere with the conclusions previously discussed. Many crude oils from the Ural-Volga region, for example, contain more than 50 percent paraffins and more than one percent sulfur. Consequently, petroleum can be highly metamorphosed and also contain a high sulfur content. At the same time, it is known that the sulfurizing of petroleum is also associated with oxidation processes.¹ It therefore follows that oxidation and processes such as sulfurization do not influence the natural evolution of petroleum significantly. However, such processes do have a strong influence on the content of the asphaltic components and sulfur and on the specific gravity and other properties of petroleum.

It must be noted that the relations described above are based on analyses of the crude oils from pools of commercial importance. But there are also

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many small accumulations of highly asphaltic oils that are usually not exploited as well as many deposits of asphalts and similar substances, and unfortunately, the chemical studies of these materials is very inadequate. When the composition of these substances has been fully ascertained, another part of the geochemical evolution of petroleum concerned with strong oxidizing conditions will be better understood.

Reference

1. Andreev, P. F., Bogomolov, A. I., Dobryanskii, A. F., Kartsev, A. A., "Prevrashcheniya nefi v prirode" (Transformation of petroleum in nature), Leningrad, Gostoptekhizdat, 1958.

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FIGURES

Figure 1.

The hydrocarbon composition of crude oils.

1 - cenozoic; 2 - mesozoic; 3 - paleozoic.

Figure 2.

The dependence of the composition of crude oils and naphtha from age.

1 - ratio "naphthenes : paraffins" in crude oils; 2 - ratio "naphthenes : paraffins" in naphtha; 3 - ratio "naphthenes : paraffins" in light ends.



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